PtCu@TiO_2 nanoparticles by low pressure plasma

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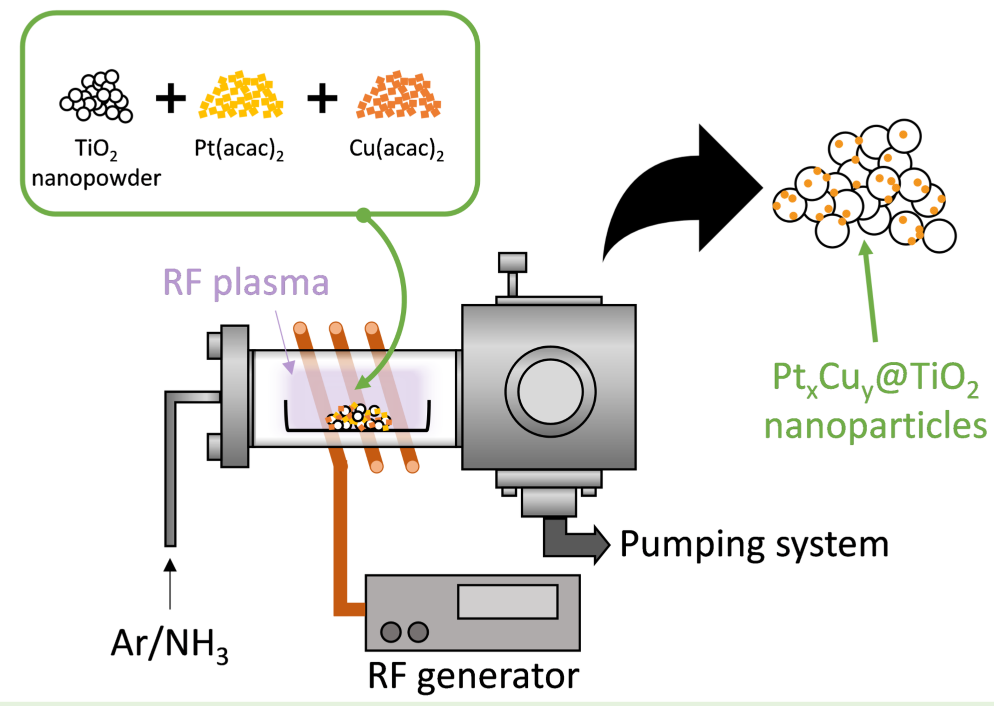
ABSTRACT

Pt based nanoparticles are widely used for application in catalysis. While most of the synthesis are based on chemical processes, involving extensive use of solvents and energy, we present here a new and original method based on the low pressure plasma process. The synthesis of Pt, Cu, and Pt_xCu_y nanoparticles (NPs) anchored onto an inorganic nanopowder substrate (TiO_2), using an Ar/NH_3 radiofrequency plasma discharge is demonstated, using solid organometallics (Cu and Pt acetylacetonate), mixed with TiO2 as starting materials. Both chemical and crystallographic characterizations confirm the formation of metastable alloyed Pt-Cu nanoparticles. The difference of Pt and Cu concentrations in NPs measured with a volume technique (X-ray diffraction) and a surface technique (X-ray photoelectron spectroscopy) suggests a Pt concentration gradient within NPs attributed to a difference in organometallics degradation kinetics.

EXPERIMENTAL METHODS

Simultaneous plasma degradation of Pt(acac)$_2$ and Cu(acac)$_2$ mixed with TiO_2 nanopowder

Figure 1: Sketch of the experimental synthesis



Raw materials:
Pt(acac)$_2$, SigmaAldrich 99.99%
Cu(acac)$_3$, SigmaAldrich 97%
TiO_2 nanopowder 100nm

Plasma discharge:
RF 13.56MHz
100W
2.5 mTorr (0.33 Pa)
Ar 4 sccm
NH_3 5 sccm
60min

Five Pt_xCu_y@TiO_2 conditions:

	wt% Pt	wt% Cu	Estimated concentration	
			at% Pt	at%Cu
Pt@TiO_2	100	0	100	0
PtCu@TiO_2 75/25	75	25	49.4	50.6
PtCu@TiO_2 50/50	50	50	24.6	75.4
PtCu@TiO_2 25/75	25	75	9.8	90.2
Cu@TiO_2	0	100	0	100

Characterizations:
XPS (250x250µm, Thermo Kalpha
TEM (Tecnai 20 and ARM 200)
XRD (X'pert Pro, θ/2θ, Cu Kα)

TEM OBSERVATIONS

Nanoparticles of 5-15 nm decorate the surface of bigger TiO_2 nanoparticles:

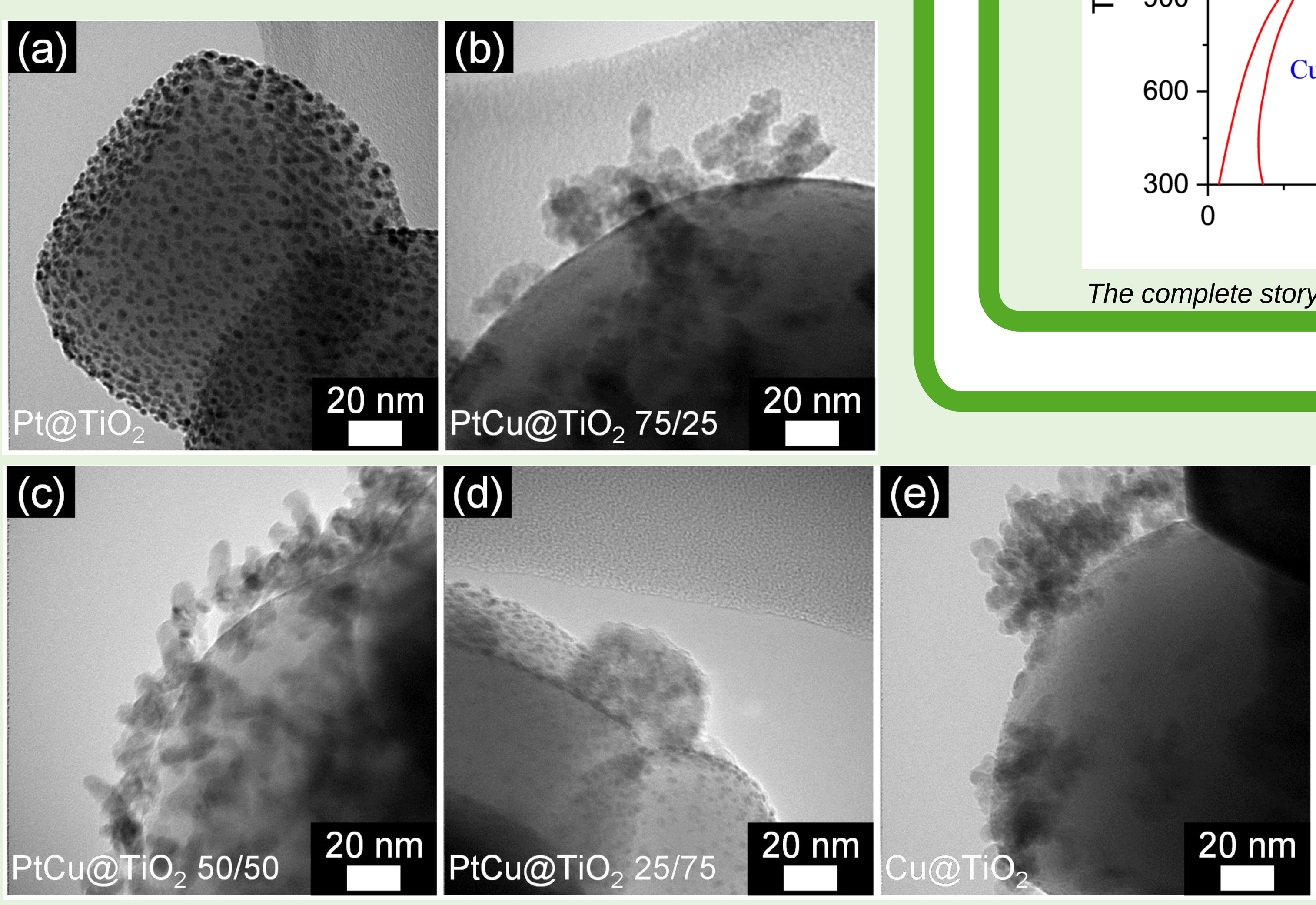
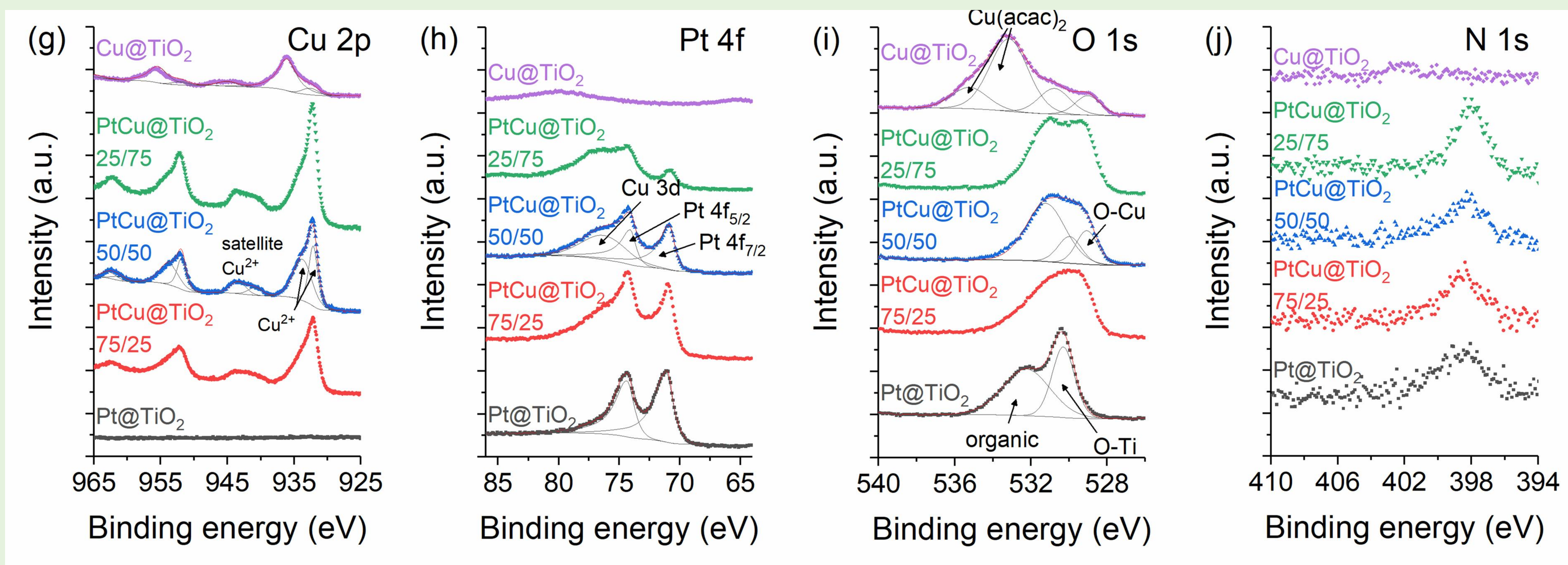


Figure 2: TEM observation of Pt_xCu_y@TiO_2 nanoparticles

NO DISTINCTION BETWEEN Pt and Cu, suggesting alloy formation

Evolution of the morphology:
Pure Pt: small and well defined nanoparticles (Fig 2.a)
Addition of copper: bigger nanoparticles (Fig 2.b, c & d)
Pure Cu: tufted morphology (Fig 2.e)

XPS ANALYSIS



Native oxide formation on Cu@TiO_2 sample (visible on O 1s and Cu 2p signal)
Almost no nitrogen reported (below 3%) even with the use of NH_3
NPs are alloyed, with a Pt concentration that is below the initial Pt concentration

Concentration derived from XPS (3 nm)

	at% Pt	at% Cu
PtCu@TiO_2 75/25	23.6	76.4
PtCu@TiO_2 50/50	13.1	86.9
PtCu@TiO_2 25/75	3.8	96.2

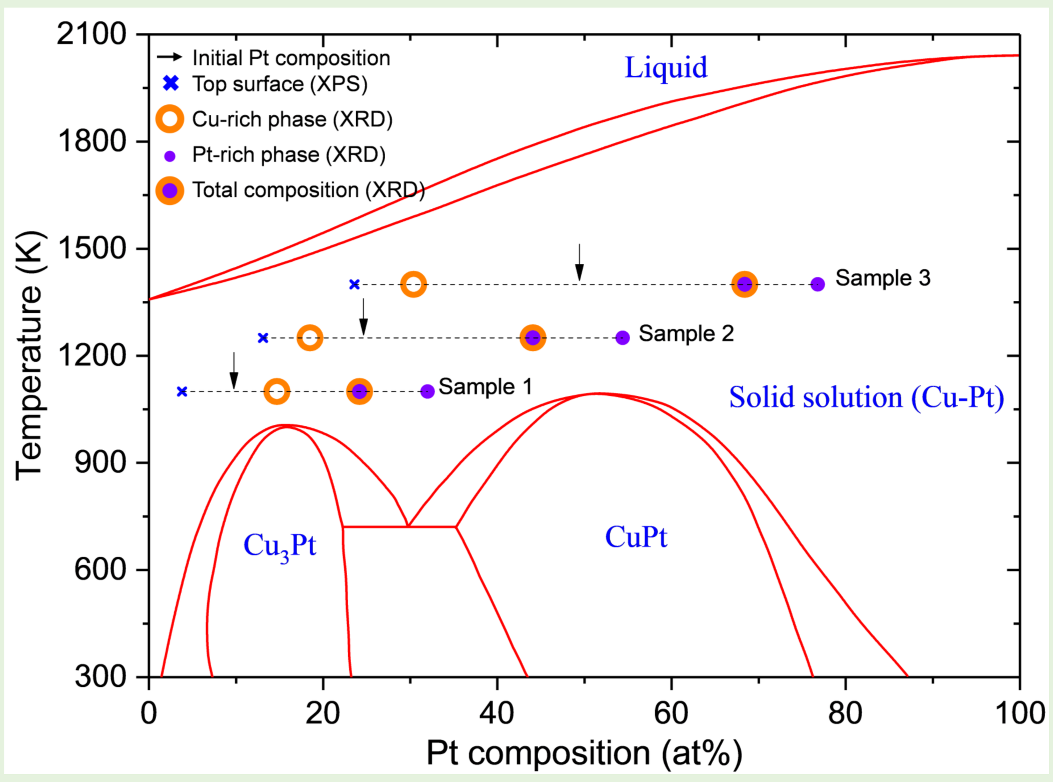
Excess of Cu
Pt is below Cu !

CONCLUSION

Successful dry synthesis of Pt, Cu, and Pt_xCu_y nanoparticles anchored onto TiO_2 nanopowder

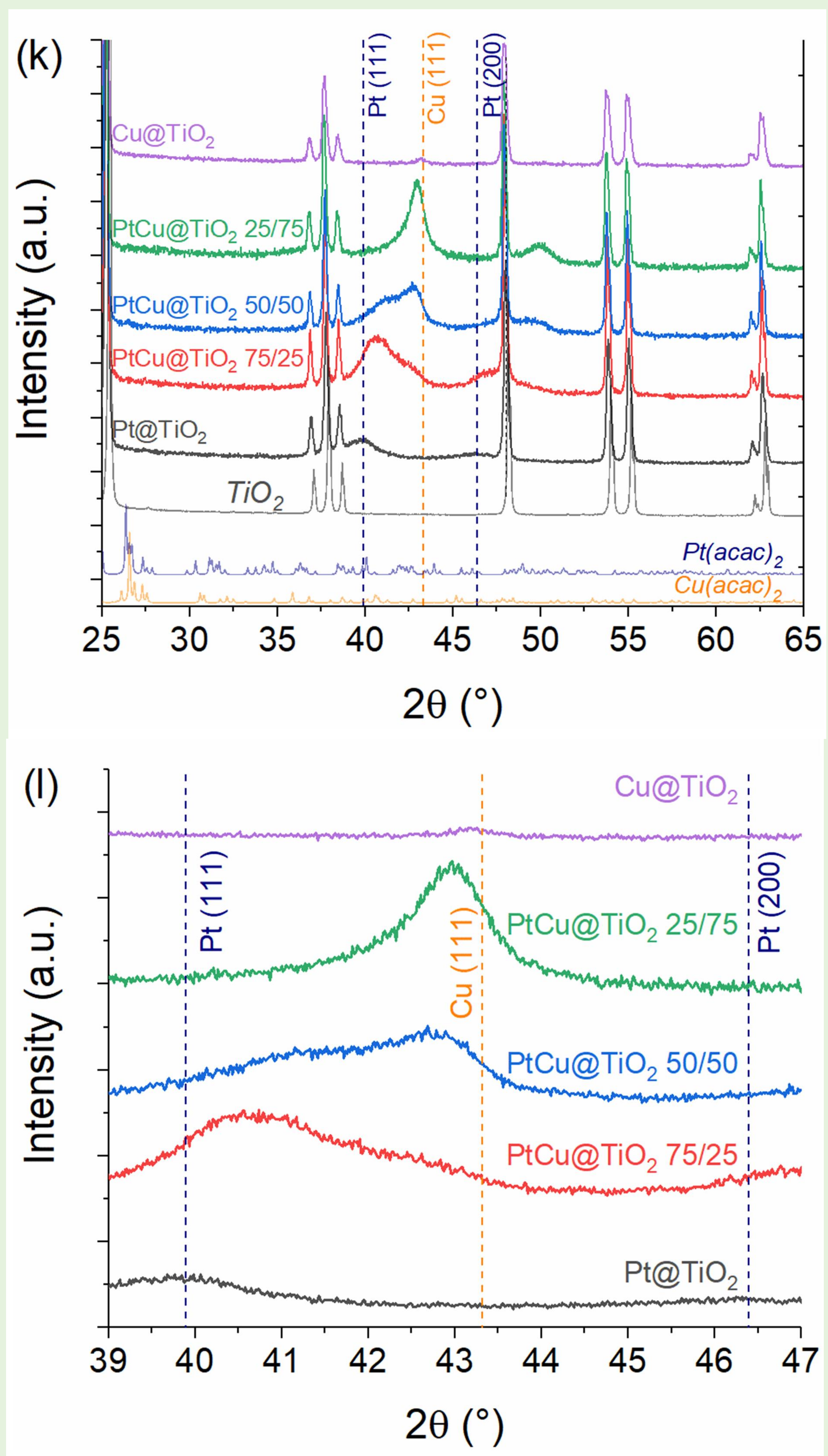
Pt-Cu alloying formation, demonstrated by XRD analysis

Pt concentration gradient within nanoparticles is suggested due to different degradation kinetics of Pt and Cu precursors



The complete story is available on doi.org/10.1016/j.matlet.2021.129576

STRUCTAL PROPERTIES



Main diffraction peak between (111) of cubic Pt and (111) of cubic Cu

Broadening of peak due to small cristallites (4-14 nm)

Expected crystallographic from phase diagram:
25/75 Cu_3Pt
50/50 Cu_3Pt + CuPt
75/25 CuPt

Experimental results:
One or two phase, with peak shifting, suggesting PtCu solid solution, whose composition is derived from Vegard law:

	at% Pt	at% Cu
PtCu@TiO_2 75/25	67.8	33.2
PtCu@TiO_2 50/50	41.8	58.2
PtCu@TiO_2 25/75	21.7	78.3

The divergence between XPS – probing the first 3 nm – and XRD – probing the entire NPs volumes – suggests heterogeneity in the Pt concentration within NPs

In accordance with stability higher stability of Cu(acac)$_2$ (Tm = 284°C) compared to Pt(acac)$_2$ (Tm = 249°C)

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Reference

Chavee et al., Materials Letters, https://doi.org/10.1016/j.matlet.2021.129576